CHAPTER 4 RESULT AND DISCUSSION

4.1 Fourier Transform Infrared Spectroscopy

4.1.1 Fourier Transform Infrared Spectroscopy of Copper(II) Cinnamate

Copper(II) cinnamate (CC) was prepared from copper(II) acetate monohydrate and cinnamic acid. The Fourier Transform Infrared (FTIR) spectra of these materials are shown in Figure 4.1. It is noted that the spectrum of CC is distinctly different from its starting materials. Thus it can be concluded that a reaction between copper(II) acetate and cinnamic acid have taken place under the experimental conditions stated in Chapter 3.

The FTIR spectrum of CC (Figure 4.1c) showed bands characteristic of its bonds and functional groups, namely C-H (aromatic), C=C (aromatic), C=C (alkene), -COO (carboxylate), C-H (alkene) and a monosubstitution pattern (Table 4.1), as indicated in the proposed structure of CC (Figure 2.9, Chapter 2) [1].

Table 4.1 FTIR data of copper(II) cinnamate

Wavenumber (cm^{-1})	Assignment
3082 - 3020	C-H (aromatic) str
1639	-C=C- (aromatic) str -COO (bridging) sym
1561 - 1492	-COO (bridging) antisym, m, str
1451 - 1403	-C=C- str, m
1251 976	-C=C- (trans) str
772 - 601	-C=C- (cis) str
772 - 687	C-H (out-of-plane deformation)
580	alkenes R'CH=CHR (cis)
484	R'CH=CHR (trans)

str- stretching , sym- symmetrical , m- medium

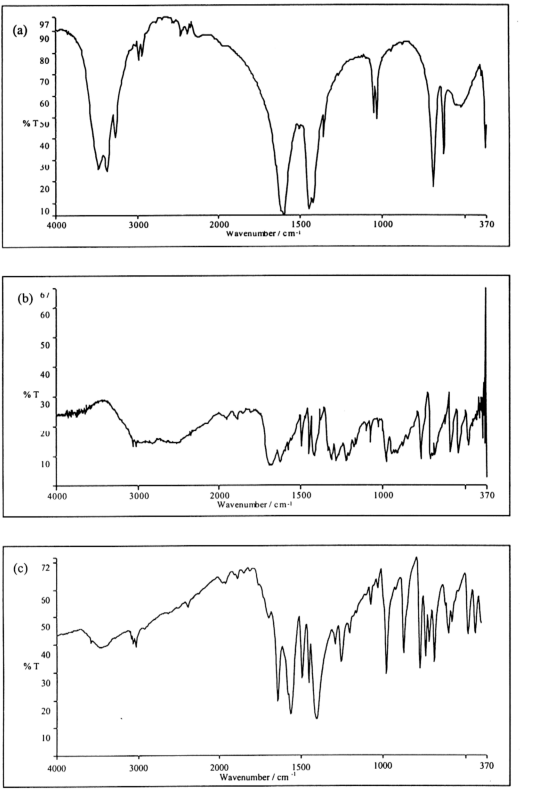


Figure 4.1 FTIR spectra of (a) copper(II) acetate monohydrate (b) cinnamic acid (c) copper(II) cinnamate

Further comparison between spectra of CC and cinnamic acid showed that some bands have shifted. For example, the band due to -COO was at 1683 cm^{-1} in cinnamic acid but shifted to lower wavenumber in CC at about 1639 cm^{-1}. This suggests that –COO in CC bonds has weaken, possibly as a result of its bonding to central copper(II) ion. The spectra also indicate that CC exists as a mixture of cis and trans isomers. The intensities of the trans band at 976 cm^{-1} and cis band at 772 cm^{-1} are almost equal, indicating that the isomers were in approximately equal amounts.

4.1.2 FTIR Spectroscopy of Copper(ll) Cinnamate Doped with Iodine

FTIR spectra of CC and CC doped with different percentage of iodine are shown in Figure 4.2. The spectra are very similar, suggesting that iodine has no detectable effect on the structure of CC. Similar observation was noted for poly(2,5-thienylene vinylene) films doped with iodine, in which it was concluded that no addition of iodine to the carbon-carbon double bonds take place [2].

Iodine was to act as oxidizing agent by removing electron(s) from CC to form CC radical cation and planar I_3^- or I_5^- counterion via complex formation [3]. This is supposed to help in the conductivity of CC. The chemical equation are as follows:

$$CC + I_2 \longrightarrow (CC)I_2$$

$$(CC)I_2 \longrightarrow [(CC)I]^+ + I^-$$

$$[(CC)I]^+ + (CC)I_2 \longrightarrow I_3^- + 2CC^+$$

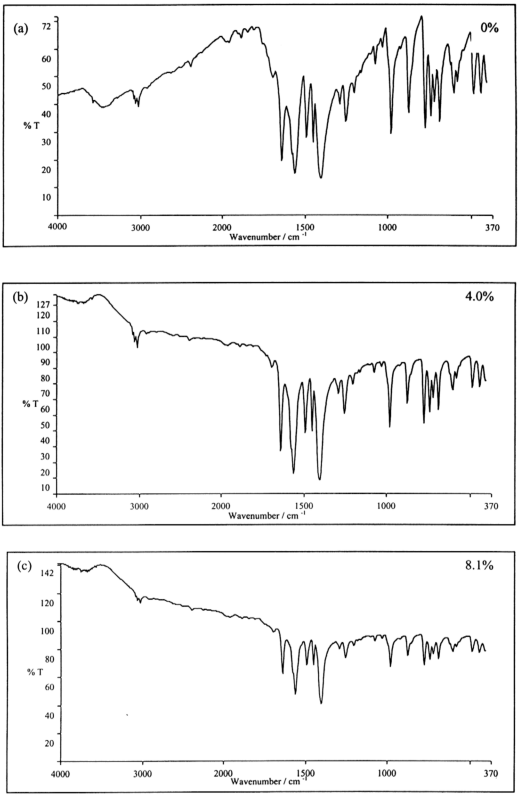
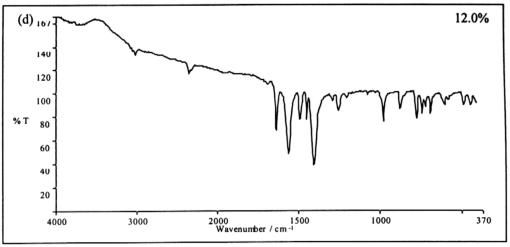
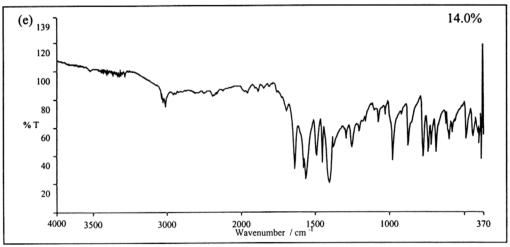


Figure 4.2 FTIR spectra of (a) copper(II) cinnamate, and (b - h) copper(II) cinnamate doped with different amount of iodine (continued)





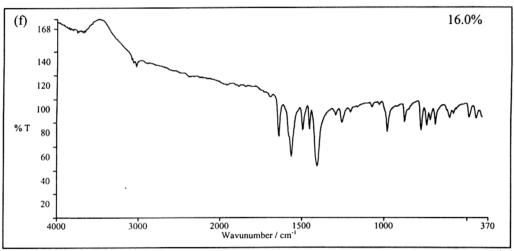


Figure 4.2 FTIR spectra of (a) copper(II) cinnamate, and (b - h) copper(II) cinnamate doped with different amount of iodine (continued)

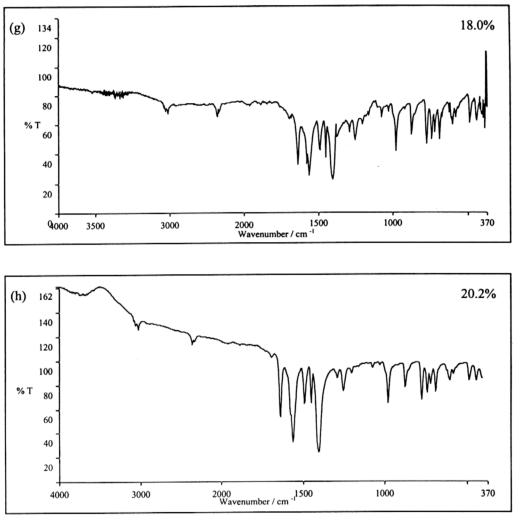


Figure 4.2 FTIR spectra of (a) copper(II) cinnamate, and (b - h) copper(II) cinnamate doped with different amount of iodine (continued)

4.1.3 FTIR Spectroscopy of Annealed Copper(II) Cinnamate

FTIR spectra of CC and CC annealed at 50°C, 100°C and 150°C are shown in Figure 4.3. The spectra are almost similar, suggesting that annealing has no effect on the structure of CC at these temperatures. Thus it may be concluded that CC is stable at this temperatures. It was observed that the color changed from light blue to black at 200°C, suggesting that it had decomposed.

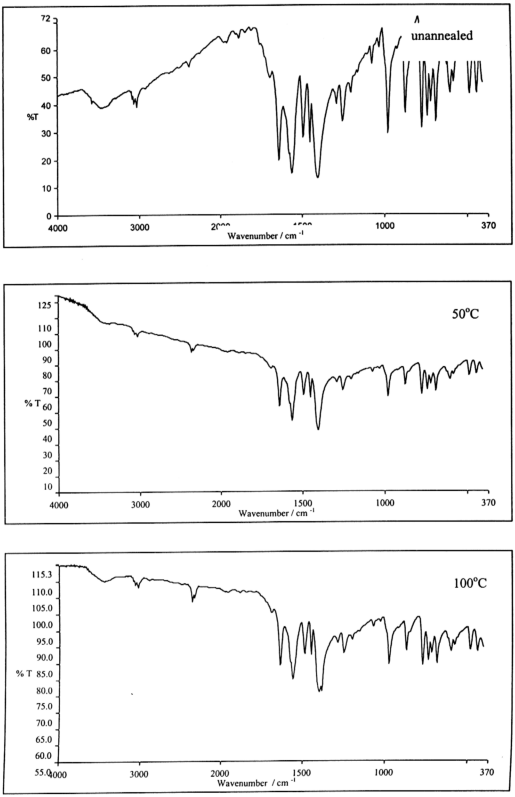


Figure 4.3 FTIR spectra of copper(II) cinnamate annealed at different temperatures

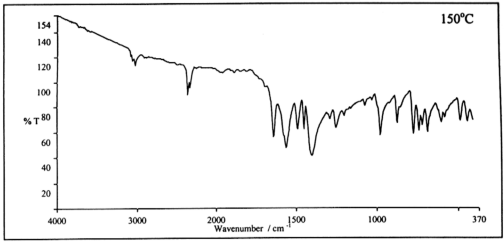


Figure 4.3 FTIR spectra of copper(II) cinnamate annealed at different temperatures (continued)

4.1.4 FTIR Spectroscopy of Annealed Copper(ll) Cinnamate Doped with 16.0% Iodine

FTIR spectra of unannealed CC doped with 16.0% iodine and CC doped with 16.0% iodine annealed at 50°C, 100°C and 150°C are shown in Figure 4.4. The spectra are almost similar, suggesting that annealing has no effect on the structure of CC doped with 16.0% iodine at these temperatures. Thus, it may be concluded that CC doped with 16.0% iodine is stable at these temperatures. It was observed that the colour of CC doped with 16.0% iodine changed from light blue to black at 200°C, suggesting that it had decomposed.

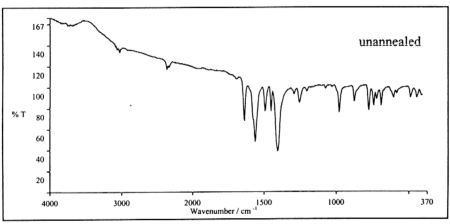
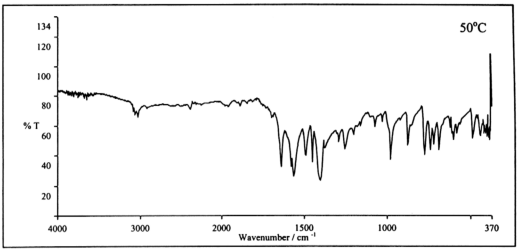
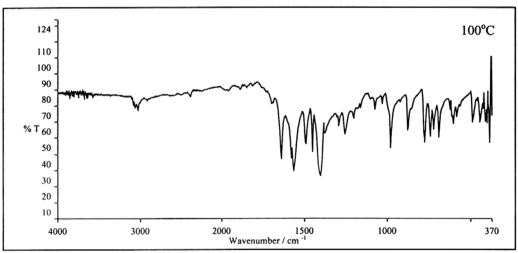


Figure 4.4 FTIR spectra of copper(II) cinnamate doped with 16.0% iodine annealed at different temperatures





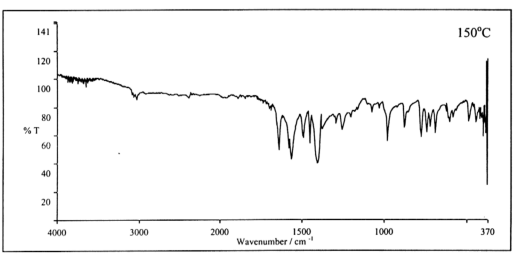


Figure 4.4 FTIR spectra of copper(II) cinnamate doped with 16.0% iodine annealed at different temperatures (continued)

4.2 Conductivity

The values of thickness T, electrode diameter D, and electrode area A for CC and CC doped with different amount of iodine are tabulated in Table 4.2 and Table 4.3 respectively.

Table 4.2 Thickness of sample

Percentage of Iodine	Thickness (T± 0.001)cm					Average ($\overline{T}$ ± 0.001)cm
	1	2	3	4	5	
0.0	0.038	0.039	0.039	0.040	0.040	0.039
4.0	0.038	0.038	0.038	0.038	0.038	0.038
8.1	0.049	0.048	0.050	0.051	0.052	0.050
12.0	0.039	0.039	0.040	0.039	0.037	0.039
14.0	0.032	0.032	0.032	0.032	0.033	0.032
16.0	0.037	0.037	0.037	0.037	0.037	0.037
18.0	0.037	0.038	0.038	0.038	0.038	0.038
20.2	0.037	0.038	0.036	0.037	0.038	0.037

Table 4.3 Diameter and area of electrode

Percentage of Iodine	Diameter (D ± 0.001)cm					Average $\overline{D}$ ± 0.001 /cm	Area A ± 0.0001 /cm^2
	1	2	3	4	5		
0.0	0.248	0.252	0.251	0.249	0.250	0.250	0.0491
4.0	0.302	0.299	0.305	0.304	0.315	0.305	0.0731
8.1	0.261	0.262	0.262	0.267	0.263	0.263	0.0543
12.0	0.320	0.331	0.325	0.321	0.328	0.325	0.0830
14.0	0.260	0.262	0.258	0.262	0.259	0.260	0.0531
16.0	0.340	0.346	0.342	0.339	0.348	0.343	0.0924
18.0	0.241	0.240	0.243	0.240	0.246	0.242	0.0460
20.2	0.270	0.260	0.260	0.252	0.260	0.260	0.0531

The conductivity of CC is given by

$$\sigma = \frac{I}{V}\frac{\overline{T}}{A} \qquad (4.1)$$

where A is the cross sectional area of the electrode, $\overline{T}$ is the average thickness of sample, V is the voltage applied across the cross sectional area and I is the current measured. Figure 4.5(a) and (b) are graphs of I versus V and log I versus log V of CC doped with 14.0% iodine.

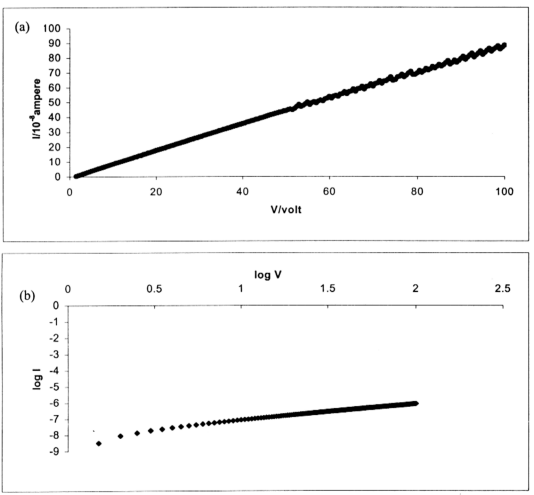


Figure 4.5 Graph of (a) I versus V (b) log I versus log V for copper(II) cinnamate doped with 14.0% iodine

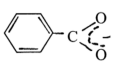
Referring to equation 4.1, I/V is the slope (m) in the ohmic region of the graph of I versus V. Equation 4.1 can be rewritten as

$$\sigma = \frac{4m\overline{T}}{\pi\overline{D}^2} \qquad (4.2)$$

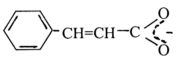
where $A = \pi\left(\frac{\overline{D}}{2}\right)^2$. The ohmic region is the region where slope of log I versus log V equals to unity. The samples studied obey the Ohm's law.

4.2.1 Conductivity of Copper(II) Cinnamate

The conductivity of CC was found to be in the range (0.52 - 0.8) x 10^{-10} Scm^{-1}. This value is about 16 times higher than the conductivity of copper(II) benzoate at 3.24 x10^{-12} Scm^{-1}[4]. The higher conductivity of CC possibly because its ligand has higher degree of conjugation compared to copper(II) benzoate, as shown in Figure 4.6. The higher conductivity of CC may also be due to less steric hindrance in its structure for both cis and trans configurations.



(a)



(b)

Figure 4.6 Structure of (a) benzoate ligand (b) cinnamate ligand

Figure 4.7 shows the variation of conductivity of CC with temperature between 300 K down to 77K. The graph indicates metallic behaviour from 86K to 285K. The data was then plotted with reference to band model (Figure 4.8) and Mott's variable range hopping (VRH) model (Figure 4.9). Graph in Figure 4.8 is not linear and with a positive gradient indicating that CC does not follow the band model from 285K to 86K.

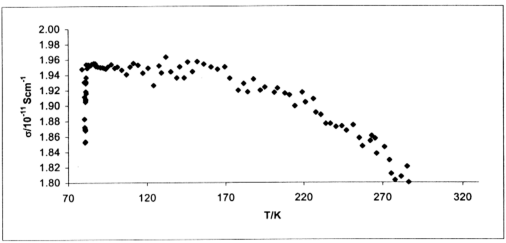


Figure 4.7 Graph of conductivity σ versus temperature T for copper(II) cinnamate

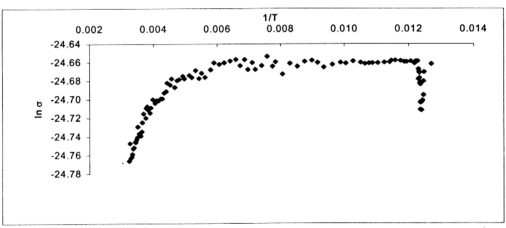


Figure 4.8 Graph of ln σ versus 1/T for copper(II) cinnamate

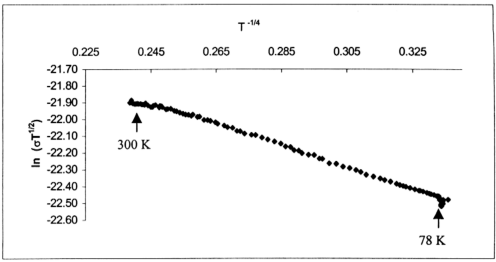


Figure 4.9 Graph of ln ($\sigma T^{1/2}$) versus $T^{-1/4}$ for copper(II) cinnamate

Graph of Figure 4.9 is linear indicating that the conduction mechanism for CC follows VRH model. The VRH parameters, namely the density of states at Fermi level, $N(E_F)$, hopping distance, R, hopping energy, ΔE and density of charge carriers, n, for CC were calculated from the following formulae as given in Chapter 2. The results are tabulated in Table 4.4

$$T_o = 18.1\alpha^3 / kN(E_F)$$

$$R = \left(\frac{9}{8\pi\alpha N(E_F)kT} \right)^{1/4}$$

$$\Delta E = \left[\frac{2\alpha^3 k^3 T^3}{9\pi N(E_F)} \right]^{1/4}$$

$$n = N(E_F)kT$$

The value of T_o was calculated from the slope, m of graph ln $\sigma T^{1/2}$ versus $T^{-1/4}$ as follows.

$$m = -\left(\frac{1}{T_o}\right)^{-1/4}$$

The value of α is assumed to be 6Å which is twice the size of polypyrrole (PPY) [5].

Table 4.4 Variable range hopping parameters of copper(II) cinnamate

T_o	1531 K
$N(E_F)$	6.35×10^{23} $eV^{-1}cm^{-3}$
R (298 K)	3.38 Å
ΔE (298 K)	0.0097 eV
n (298 K)	1.63×10^{28} cm^{-3}

The values of $N(E_F)$, R, ΔE at 298K for CC may be compared with values reported for iodine doped (0.033M) poly(2,5-thienylene vinylene), PTV at the same temperature which are 7.6×10^{20} $eV^{-1}cm^{-3}$, 17 Å, and 0.06 eV respectively [2].

4.2.2 Conductivity of Copper(II) Cinnamate Doped with Different Percentage of Iodine

The conductivity calculated for CC doped with different percentages of iodine are tabulated in Table 4.5. The graph of conductivity versus percentage of iodine for CC is shown in Figure 4.10. The graph shows that the conductivity increase gradually up to a maximum value at 16.0% iodine. The highest conductivity obtained was 4.82×10^{-9} Scm^{-1} and is about 90 times higher compared to CC. The increase in conductivity of CC in the presence of 16.0% iodine may be due to the oxidizing effect of iodine resulting in the formation of vacant energy level. It is also due to the decrease in hopping distance from 3.38 Å to 3.02 Å

in CC doped with 16.0% iodine and thus reducing the activation energies. The carriers can then hopped easily from one energy level to the other.

Table 4.5 Conductivity of copper(II) cinnamate doped with different percentage of iodine

Percentage of Iodine	Conductivity, σ /10^{-10} Scm^{-1}			
	Before empty trap		After empty trap	
	Forward	Reverse	Forward	Reverse
0.0	0.76	0.80	0.52	0.60
4.0	1.85	0.10	0.13	0.24
8.1	25.30	24.86	7.04	7.50
12.0	29.00	36.92	39.50	12.50
14.0	53.00	54.41	37.50	39.48
16.0	84.20	94.50	48.20	46.40
18.0	17.80	19.77	14.00	16.27
20.2	7.80	8.77	0.20	24.66

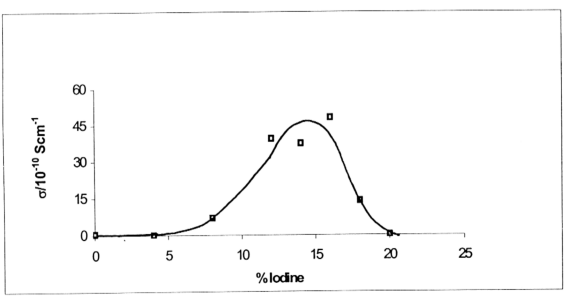


Figure 4.10 Conductivity of copper(II) cinnamate doped with different percentage of iodine (after empty trap, forward)

Figure 4.11 shows that the variation of conductivity with temperature for CC doped with 16.0% iodine between 78K to 300K. The graph indicates metallic behaviour. The data was then plotted with reference to band model (Figure 4.12) and Mott's variable range hopping (VRH) model (Figure 4.13). Graph in Figure 4.12 has a positive gradient indicating that the conduction mechanism of CC doped with 16.0% iodine does not follow the band model in the entire temperature range studied.

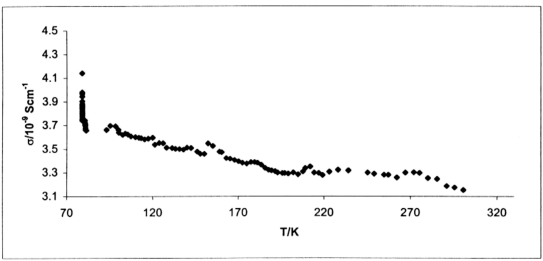


Figure 4.11 Graph of conductivity σ versus temperature T for copper(II) cinnamate doped with 16.0% iodine

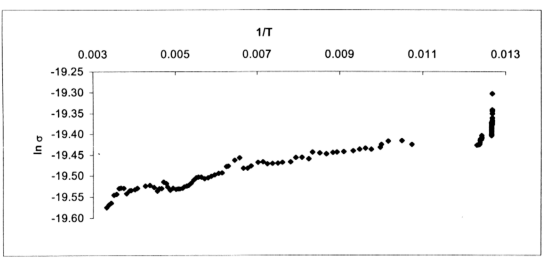


Figure 4.12 Graph of ln σ versus 1/T for copper(II) cinnamate doped with 16.0% iodine

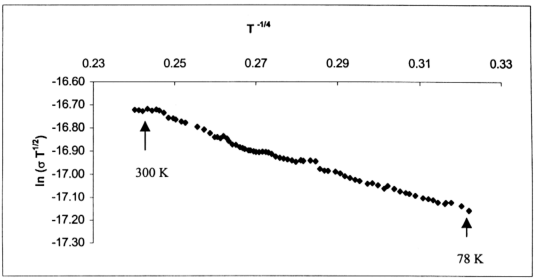


Figure 4.13 Graph of ln ($\sigma T^{1/2}$) conductivity versus $T^{-1/4}$ for copper(II) cinnamate doped with 16.0% iodine

Graph of Figure 4.13 is linear indicating that the conduction mechanism for CC doped with 16.0% iodine follows VRH model. The VRH parameters, namely the density of states at Fermi level, $N(E_F)$, hopping distance, R, hopping energy, ΔE and density of charge carriers, n, for CC doped with 16.0% iodine were calculated from the same formulae for the case of CC as given in Chapter 2. The results are tabulated in Table 4.6

Table 4.6 Variable range hopping parameters of copper(II) cinnamate doped with 16.0% iodine

T_o	969 K
$N(E_F)$	1.00×10^{24} $eV^{-1}cm^{-3}$
R (298K)	3.02 Å
ΔE (298K)	0.0087 eV
n (298K)	2.57×10^{28} cm^{-3}

The value of $N(E_F)$, R, ΔE for CC at 298K can be compared with values reported for poly(2,5-thienylene vinylene), PTV doped with 0.405M iodine at the same temperature which are 16.3×10^{20} $eV^{-1}cm^{-3}$, 14 Å, and 0.05 eV respectively [2].

4.2.3 Effect of Annealing on the Conductivity of Copper(II) Cinnamate and Copper(II) Cinnamate doped with 16.0% Iodine

CC and CC doped with 16.0% iodine were annealed at 50°C, 100°C, 150°C and 200°C. FTIR not done on sample doped with 16.0% iodine annealed at 200°C. The graphs of conductivity versus annealing temperature for both samples are shown in Figure 4.14. It was observed that both samples shows no significant change in conductivity for all annealing temperatures. The FTIR results for both samples also shows no significant new peaks in the annealing process up to 150°C. It can be concluded that CC and CC doped with 16.0% iodine was quite stable up to 150°C. It was observed that the color of CC and CC doped with 16.0% iodine change from light blue to black at 200°C.

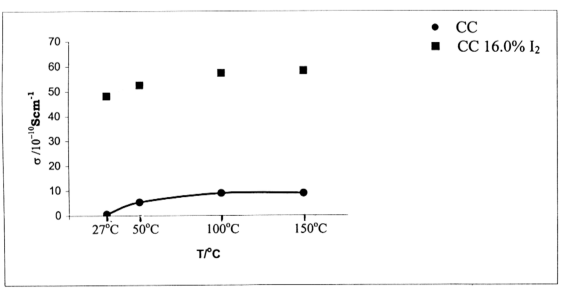


Figure 4.14 Graph of conductivity of copper(II) cinnamate and copper(II) cinnamate doped with 16.0% iodine annealed at different temperatures

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